

# Chromatographic properties of tetramethyl-*p*-silphenylene–dimethyl, diphenylsiloxane copolymers as stationary phases for gas–liquid chromatography

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## Abstract

Seven tetramethyl-*p*-silphenylene–dimethyl, diphenylsiloxane copolymers were coated on fused-silica capillary columns to evaluate their properties as stationary phases in gas–liquid chromatography. The capillary columns were tested concerning their selectivity, separation efficiency, column bleed, inertness, elution temperatures, and working range. The following characteristic properties of the silphenylene unit were found: (i) the impact of the silphenylene group on the chromatographic selectivity is similar to that of two dimethylsiloxy groups and half of a diphenylsiloxy group; (ii) silphenylene-siloxane copolymers offer reduced column bleed and increased maximum allowable operating temperature in comparison to polysiloxanes, since the backbone stiffening phenylene group enhances thermal stability; (iii) the elution temperatures of analytes are increased by 15–30 °C on silphenylene-siloxane copolymers compared to polysiloxanes; (iv) the silphenylene unit increases the glass transition temperature of the polymers resulting in elevated minimum allowable operating temperatures.

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## 1. Introduction

Due to their excellent thermal properties and their wide variety of applicable substituents polysiloxanes are extensively used as stationary phases in gas–liquid chromatography. The high thermal and chemical stability is additionally improved by backbone

stiffing groups, which are inserted into the polysiloxane chain. Steric hindrance restricts the formation of cyclic degradation products resulting in reduced column bleed. Today, almost every column supplier offers low-bleed or MS capillary columns based on the so-called silarylene technique. Due to their superior properties these capillary columns replace partly the conventional polysiloxane stationary phases. Low-bleed columns are claimed to be equivalent to conventional polysiloxanes, although some differences regarding the selectivity were reported

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[1–3]. Unfortunately, no or only limited information concerning the chemical nature of the stationary phase or the column technology is provided by the manufacturers [4,5]. Aside of carborane and tetramethyl-*p,p'*-sildiphenylene ether units, the tetramethyl-*p*-silphenylene unit is apparently the most commonly used backbone stiffing group. A 50% silphenylene–50% methylphenylsiloxane copolymer has been applied as stationary phase in fused-silica capillary columns up to 360 °C by Buijten et al. [6]. The same working group has prepared a cyanopropyl containing silphenylene-siloxane copolymer and characterized it for GC applications [7]. The synthesis, coating, and column characterization of silphenylene-dimethyl, methylphenyl, and diphenylsiloxane copolymers have been described by several authors [8–12]. Aichholz and co-workers have used glass capillary columns for the analysis of triacylglycerols and polyaromatic compounds and demonstrated that even a maximum allowable operating temperature of 430 °C was possible [11,12].

Only a few reports dealt with the characterization of commercially available capillary columns based on silarylene chemistry. Low bleed rates of silphenylene polymers as specified by the manufacturers have been confirmed for three capillary columns [1]. Slightly deviating selectivities have been reported for silphenylene containing stationary phases which are claimed to be equivalent to 95% dimethyl, 5% diphenyl-polysiloxane [2,3].

In a previous paper the synthesis and NMR characterization of silphenylene-dimethyl, diphenylsiloxane copolymers have been described [13]. In this work, these copolymers are characterized as gas chromatographic stationary phases coated to fused-silica capillary columns in regard to selectivity, column bleed, thermal stability, operating temperatures, and elution temperatures.

## 2. Experimental

### 2.1. Reagents and materials

The monomers bis(dimethylamino)dimethylsilane, bis(dimethylamino)diphenylsilane, diphenylsilanediol, and 1,4-bis(hydroxydimethyl-silyl)benzene were supplied from ABCR (Karlsruhe, Germany). The

stationary phase SOP-75 (74.4% diphenyl, 25.6% dimethyl-polysiloxane) was prepared and coated on fused-silica capillaries as described recently [5]. The capillary 007-65HT coated with a 65% diphenyl, 35% dimethyl-polysiloxane (15 m, 0.32-mm I.D., 0.1- $\mu$ m film thickness) was purchased from Quadrex Corporation (Woodbridge, CT). The capillary DB-1ht (100% dimethyl-polysiloxane, 15 m, 0.32-mm I.D., 0.1- $\mu$ m film thickness) was obtained from Agilent Technologies (Palo Alto, CA).

The test mixture for polar capillary columns according to Grob et al. [14,15], the components for the extended Donike test mixture [11,16], the C<sub>6</sub>–C<sub>11</sub> *n*-alkane reference solutes, and the first five Rohrschneider–McReynolds standards were obtained from Fluka (Buchs, Switzerland). The components of the triacylglycerol test mixture and cholesteryl dodecanoate were purchased from Sigma (St. Louis, MO).

### 2.2. Stationary phase synthesis and characterization

As described recently, a series of methoxy-terminated tetramethyl-*p*-silphenylene–dimethyl, diphenylsiloxane copolymers was prepared and characterized by nuclear magnetic resonance (NMR) spectroscopy [13]. Briefly, a condensation reaction between diaminosilanes and silandiols was used to prepare high-molecular mass polymers. The chemical composition and microstructure of the copolymers were determined by <sup>1</sup>H and <sup>29</sup>Si NMR spectroscopy. Almost perfectly alternating microstructures were found for SM-50 and SP-50, whereas the other phases were intermediates between alternating and randomized copolymers. Abbreviations of the copolymers and their chemical composition are given in Table 1. The glass transition temperature of the copolymers was determined by a differential scanning calorimetry (Pyris 7, Perkin-Elmer Instruments, Norwalk, CT).

### 2.3. Capillary preparation

The capillary columns were prepared as recently described [5,13,17,18]. Fused-silica tubes with 0.32-mm I.D. (Polymicro Technologies, Phoenix, AZ) were consecutively leached at 100 °C with sodium

Table 1  
Abbreviations of seven silphenylene-siloxane copolymers and their chemical composition (mol%) determined by  $^{29}\text{Si}$  NMR spectroscopy [13]

Polymer	Silphenylene	Dimethyl	Diphenyl
SM-30	29.2	70.8	0.0
SM-50	45.3	54.7	0.0
SP-50	51.4	0.0	48.6
SP-43	45.3	0.0	54.7
SP-25	25.7	0.0	74.3
SP-20	24.4	0.0	75.6
SMP-5	7.4	22.0	70.6

hydroxide and hydrochloric acid. After drying at 230 °C, the capillaries were flushed with 1,3-dimethyl-1,1,3,3-tetraphenyldisilazane (Fluka) dissolved in dichloromethane. The solvent was removed and the capillaries were deactivated for 12 h by high-temperature silylation at 380 °C [19]. Static coating was performed with a 0.25% (w/v) solution of the stationary phase in dichloromethane–pentane resulting in a film thickness of 0.20  $\mu\text{m}$ . Finally, the capillaries were conditioned in the gas chromatograph at 300 °C for 5 h and at 350 and 380 °C for 3 h, respectively.

#### 2.4. Capillary evaluation

All analyses were performed on a Hewlett-Packard gas chromatograph 5890 Series II equipped with a flame ionization detector (Agilent Technologies, Palo Alto, CA). Hydrogen with a purity of >99.9999% was used as carrier gas at a constant flow of 0.50 m/s. One- $\mu\text{l}$  aliquots of the test mixtures were introduced via cold-on-column injection. The flame ionization detector (FID) was operated 20 °C above the final oven temperature. The Grob test mixture for polar columns was injected at 40 °C and temperature-programmed at a rate of 4°/min to 160 °C [14,15]. The extended Donike test mixture was used to evaluate the inertness of the capillary surface [11,16] and to determine the elution temperature of the *n*-alkane  $\text{C}_{34}$ . The mixture was injected at 50 °C and temperature-programmed at a rate of 4°/min to 320 °C. A triacylglycerol (TAG) test mixture was used to evaluate the chromatographic properties of

the capillaries at high-temperatures such as selectivity, polarity, separation efficiency, and inertness [18]. The mixture was injected at 60 °C, temperature-programmed at a rate of 25°/min to 280 or 300 °C followed by a rate of 4°/min to a final temperature of 380–400 °C. For calculating of TAG-indices, a calibration curve was generated with the saturated triacylglycerols tripalmitin (PPP, 3×C16:0), tristearin (SSS, 3×C18:0), triarachidin (AAA, 3×C20:0), tribehenin (BeBeBe, 3×C22:0), and trilignocerin (LgLgLg, 3×C24:0). The polyunsaturated triacylglycerols triolein (OOO, 3×C18:1, CN 54:3), trilinolein (LLL, 3×C18:2, CN 54:6), and trilinolenin (LnLnLn, 3×C18:3; CN 54:9) served as test analytes to monitor the analyte–stationary phase interactions. A cholesteryl fatty acyl ester, cholesteryl dodecanoate, CE12:0, was used to determine the elution temperature and was analyzed under the same chromatographic conditions as the TAG test mixture.

The Kováts retention indices of the first five Rohrschneider–McReynolds standards benzene, 1-butanol, 2-pentanone, 1-nitropropane, and pyridine were measured at 60 °C applying split injection [20,21]. The gas hold-up time corrected with the phase ratio  $\beta/(\beta+1)$  was determined with methane [22]. The average polarity of the stationary phase was expressed as the CP-index and was calculated from the sum of the first five Rohrschneider–McReynolds constants divided by the sum of the Rohrschneider–McReynolds constants of OV-275 multiplied by 100 [23].

The determination of the minimum allowable operating temperature (MiAOT) of a capillary was based on the peak shape and peak height of early eluting components of the Grob and Donike test mixtures [5]. The maximum allowable operating temperature (MAOT) was deduced from data concerning the inertness and separation efficiency of the capillary columns after conditioning up to 390 °C. The separation efficiency was expressed as Trenzahl values (TZ) established at low temperatures for the fatty acyl methyl esters  $E_{10}/E_{11}$  and  $E_{11}/E_{12}$  of the Grob test mixture [24]. At elevated temperatures the TZ values were determined with the *n*-alkanes  $\text{C}_{26}/\text{C}_{30}$  and  $\text{C}_{30}/\text{C}_{34}$  of the Donike test mixture, whereas each TZ represented a mean value of four different TZ values.

### 3. Results and discussion

#### 3.1. Selectivity

A direct comparison of the silphenylene-siloxane copolymers with other stationary phases was achieved with the Grob test mixture (Fig. 1). The respective chromatograms of the silphenylene-siloxane copolymers are similar to those of polysiloxanes with low to intermediate polarity, as already described in the literature [5,17,25,26] or by the suppliers of capillary columns. In this context, the Grob test chromatogram of the apolar phases SM-30 and SM-50 resemble to those of a 25% silphenylene, 75% dimethylsiloxane-copolymer and a 33% silphenylene, 67% dimethylsiloxane-copolymer coated to glass capillaries [11]. The elution temperatures of apolar components such as *n*-alkanes or fatty acid methyl esters decrease with increasing polarity of the stationary phase. On the other side, an aromatic compound (2,6-dimethylaniline, A) is more retarded.

A universal system to characterize the selectivity of a stationary phase is the concept of Rohrschneider [20] and McReynolds [21]. The sum of the Rohrschneider–McReynolds constants expressed as CP-index has earlier been used to calculate the average polarity of the stationary phases [23]. The Rohrschneider–McReynolds constants of seven silphenylene-siloxane copolymers are summarized in Table 2. Furthermore, the Rohrschneider–McReynolds constants of 21 commercial dimethyl, diphenyl-polysiloxanes were either taken from the literature [21], from specifications of the manufacturers, or were directly measured (DB-1ht and SOP-75). The respective CP-indices of these dimethyl, diphenyl-polysiloxanes are plotted against their diphenyl content giving evidence of a relationship between diphenyl content and CP-index (Fig. 2). Methylphenyl, diphenyl-polysiloxanes, as e.g., OV-17, OV-22 and OV-25, do not fit in the regression curve, since they exhibit distinctly lower CP-indices compared to dimethyl, diphenyl-polysiloxanes. This graph can be used to evaluate the influence of the silphenylene unit on the stationary phase polarity. All seven silphenylene-siloxane copolymers lay roughly on this regression curve, when the calculation of the equivalent diphenyl content is based on the assumption that one silphenylene unit is identical

with two dimethylsiloxy groups and one-half of a diphenylsiloxy group (see Section 3.2). However, the impact of the silphenylene unit on the CP-index is slightly overestimated with this model.

Unfortunately, the significance of the Rohrschneider–McReynolds constants is restricted to analyte–stationary phase interactions at moderate temperatures. Additional parameters are required to describe the interactions at elevated temperatures, since temperature induced dipoles may change the selectivity. Therefore, the TAG-indices of the polyunsaturated TAGs OOO, LLL, and LnLnLn were introduced to describe the interactions between the analytes and the stationary phase at high-temperatures (see Section 2). A linear relationship between the elution temperatures of homologous series of saturated TAGs (PPP, SSS, AAA, BeBeBe, LgLgLg) versus their carbon number (CN 48–72) as well as their molecular mass was found with correlation coefficients of  $R > 0.9995$  for all investigated stationary phases. The polyunsaturated triacylglycerols OOO, LLL, and LnLnLn served as probes to investigate the interactions between the probes and the stationary phase at high temperatures. The TAG-indices are a descriptive parameter for the interactions as they specify that carbon number (CN) at which an analyte elutes from the column. For example, a TAG-index of 56 for LLL indicates that LLL co-elutes with the saturated triacylglycerol SSA on a given phase.

The TAG-index established for LnLnLn can be used to rank stationary phases according to their degree of polarity. Phases that provide values below 55 are considered apolar, e.g., 100% dimethyl-polysiloxanes or 95% methyl, 5% phenyl-polysiloxanes. Values between 55 and 60 indicate intermediate polar stationary phases. Highly polar stationary phase, as, e.g., phases with cyanopropyl groups, are expected to provide values over 60. The TAG-indices of several popular methyl, phenyl-polysiloxanes and seven silphenylene-siloxane copolymers are summarized in Table 3. All five silphenylene-diphenylsiloxane copolymers are of intermediate polarity, whereas the silphenylene-dimethylsiloxane copolymers SM-30 and SM-50 are of low polarity. It is remarkable that the TAG-index of SM-50 exceeds the values of 100% dimethyl-polysiloxanes and 95% dimethyl, 5% diphenyl-polysiloxanes which is obviously caused by

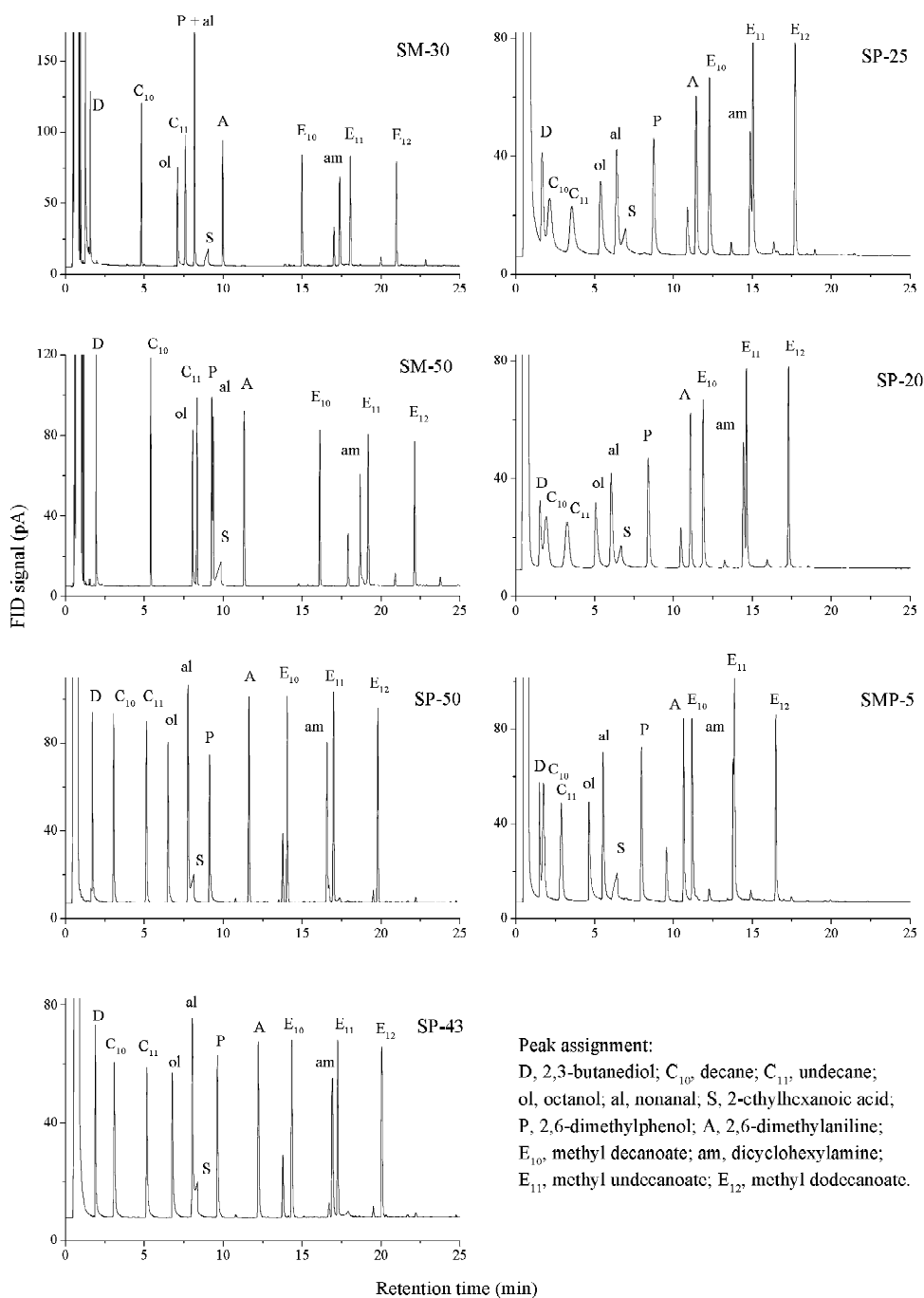


Fig. 1. Chromatograms of the test mixture for polar stationary phases according to Grob of seven silphenylene-dimethyl, diphenylsiloxane copolymers. Capillary columns: 15 m, 0.32-mm I.D., 0.20- $\mu$ m film thickness, after conditioning up to 380 °C. Temperature program: 40–140 °C at 4 °/min; 0.50 m/s hydrogen linear velocity.

Table 2  
The Rohrschneider–McReynolds constants and CP-indices of seven silphenylene-siloxane copolymers

Stationary phase	Benzene	<i>n</i> -Butanol	2-Pentanone	Nitropropane	Pyridine	CP-index
SM-30	25.8	85.7	77.6	116.5	64.1	8.9
SM-50	33.9	94.4	84.0	131.4	77.8	10.1
SP-50	106.4	161.3	154.7	228.6	179.0	19.9
SP-43	113.8	161.3	163.2	241.6	193.5	20.9
SP-25	154.2	189.8	195.4	280.7	241.3	25.4
SP-20	155.3	191.3	196.3	284.5	248.3	25.8
SMP-5	162.9	199.4	204.5	296.4	265.1	27.0

the  $\pi$ – $\pi$  interactions between the phenylene group and the probes.

The plot of TAG-indices of OOO, LLL, and LnLnLn versus the phenyl content of dimethyl, diphenyl-polysiloxanes OV-1, SE-52, SOP-50, and SOP-75 is given in Fig. 3. The obtained calibration curves offer regression coefficients of  $>0.998$  for OOO, LLL, and LnLnLn, respectively. Also in this case, methylphenyl-polysiloxanes such as OV-22, 007-65HT or OV-25 were excluded, as their TAG-indices are below those of dimethyl, diphenyl-polysiloxanes.

Fig. 3 may be used to evaluate the influence of the silphenylene group on the overall polarity of the stationary phase, when the equivalent phenyl content is calculated with the assumption that one silphenylene unit corresponds to two dimethylsiloxo and one-half of a diphenylsiloxo group. With this calculation of the equivalent diphenyl content the TAG-indices of the silphenylene-siloxane copolymers are in good agreement with the linear regression curves of the dimethyl, diphenyl-polysiloxane TAG-indices, giving evidence that the proposed equivalence model fits well with experimental data.

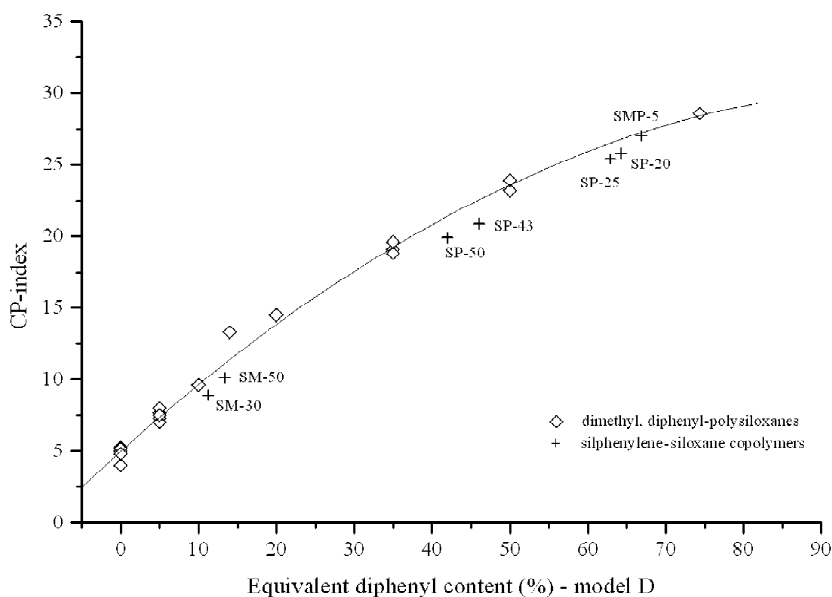


Fig. 2. CP-index versus diphenyl content of capillary columns coated with 21 commercially available dimethyl, diphenyl-polysiloxanes ( $\diamond$ ). Seven silphenylene-siloxane copolymers (+) were plotted against their equivalent phenyl content that was calculated after model D: one silphenylene unit is equivalent to two dimethylsiloxo and one-half diphenylsiloxo group.

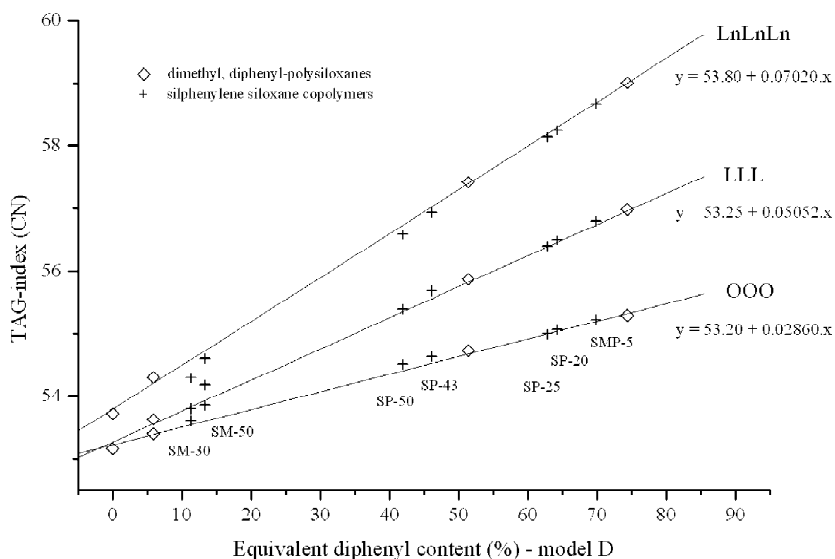


Fig. 3. TAG-indices of OOO, LLL, and LnLnLn versus diphenyl content of four dimethyl, diphenyl-polysiloxanes, OV-1, SE-52, SOP-50, and SOP-75 ( $\diamond$ ) connected with a linear regression line. The TAG-indices of seven silphenylene-siloxane copolymers (+) are plotted against their equivalent diphenyl content calculated after model D.

### 3.2. Equivalence model

Four models are feasible to calculate the contribution of the silphenylene unit to the overall selectivity

of a stationary phase, see Table 4. These models were evaluated with experimental data which were either graphically determined from the CP-index in Fig. 2 or calculated from the TAG-indices of di-

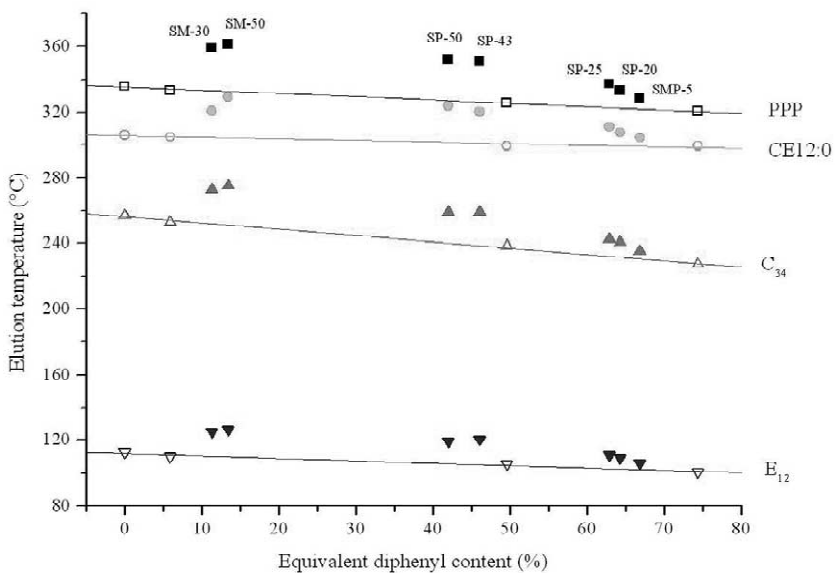


Fig. 4. Elution temperatures of E<sub>12</sub>, C<sub>34</sub>, CE12:0, and PPP versus the diphenyl content of four dimethyl, diphenyl-polysiloxanes, OV-1, SE-52, SOP-50, and SOP-75 (open symbols) connected with linear regression curves. The elution temperatures of seven silphenylene-siloxane copolymers (solid symbols) were plotted against their equivalent diphenyl content calculated after model D.

Table 3  
TAG-indices and chemical composition of several wide-spread methyl, phenyl-polysiloxanes and seven silphenylene-siloxane copolymers

Stationary phase	Phenyl content (mol%) <sup>a</sup>	TAG-index		
		OOO	LLL	LnLnLn
OV-1	0.0	53.16	53.16	53.72
SE-52	5.9	53.40	53.63	54.30
OV-17	50.0	54.26	55.25	56.54
SOP-50	51.4	54.73	55.87	57.42
007-65HT	65.0 <sup>b</sup>	54.88	56.17	57.86
SOP-75	74.4	55.29	56.98	59.01
SM-30		53.61	53.80	54.29
SM-50		53.85	54.18	54.60
SP-50		54.51	55.39	56.58
SP-43		54.63	55.68	56.93
SP-25		54.99	56.39	58.14
SP-20		55.06	56.49	58.25
SMP-5		55.22	56.80	58.67

<sup>a</sup> Determined by NMR [5,30].

<sup>b</sup> Given by the manufacturer.

methyl, diphenyl-polysiloxanes in Fig. 3. Model A is based on the oversimplifying assumption, that a silphenylene unit is identical with one dimethylsiloxy group. Equivalent phenyl contents of silphenylene-dimethylsiloxy copolymers were found to be too low compared to experimental data indicating a certain contribution of the silphenylene unit to the overall polarity. On the other side a too high equivalent diphenyl content was found for silphenylene-diphenylsiloxy copolymers, e.g., for SP-20. Model B is based on the assumption that a silphenylene unit is equivalent to two dimethylsiloxy groups, which implies that the phenylene ring has no impact on the polarity. Expectedly, calculated polari-

ty values were below the experimental data, especially for SM-30 and SM-50. The influence of the phenylene ring is overestimated with model C, where a silphenylene unit is assumed to be equal to two dimethylsiloxy and one diphenylsiloxy group. Finally, calculated data for the equivalent diphenyl content are in close agreement with the experimental data, when a silphenylene unit is assumed to be equivalent to two dimethylsiloxy and one-half of a diphenylsiloxy group (model D). This model yields a reliable estimate for the equivalent diphenyl content and the overall polarity and was used for the calculations in Figs. 2–4.

It is obvious that the equivalent diphenyl content derived from the CP-index is approximately 10% below the values calculated from the TAG-indices. This difference can be attributed to the temperature induced dipole of the phenylene group at elevated temperatures leading to a higher polarity and, consequently, to an apparently higher equivalent phenyl content.

Although the calculated data correspond very well to the experimental data, there is a limitation of the equivalence model D. Commercially available silphenylene-siloxane copolymers are claimed to have similar, but not identical properties as methyl, phenyl-polysiloxanes. In particular, size–shape interactions of the planar phenylene group with the analytes are disregarded by this model. For example, planar xylene isomers can gain closer physical proximity to the backbone and interact more strongly with a silphenylene-dimethylsiloxy copolymer than with a polysiloxane [3]. In general, silphenylene-siloxane copolymers are less cohesive and more hydrogen-bond basic than methyl, phenyl-polysilox-

Table 4  
Equivalent diphenyl contents of seven silphenylene-siloxane copolymers calculated with four different models, derived from the CP-index, and calculated from the TAG-indices

Stationary phase	Calculated after model				Derived from CP-index	Calculated from TAG-indices		
	A	B	C	D		OOO	LLL	LnLnLn
SM-30	0.0	0.0	18.4	11.3	8.4	14.3	10.9	7.0
SM-50	0.0	0.0	31.2	13.4	11.0	22.6	18.5	11.5
SP-50	48.6	32.1	49.3	42.0	37.0	45.7	42.3	39.6
SP-43	54.7	37.6	52.5	46.1	40.4	50.0	48.1	44.6
SP-25	74.3	57.7	66.1	62.9	57.9	62.5	62.2	61.8
SP-20	75.6	60.8	67.2	64.3	59.6	64.9	64.1	63.5
SMP-5	70.6	65.7	67.9	66.9	65.8	70.6	70.3	69.4



Table 5  
Separation efficiencies expressed as Trennzahl (TZ) of seven silphenylene-siloxane copolymers and three polysiloxanes<sup>a</sup>

Stationary phase	TZ derived from Grob test		TZ derived from Donike test	
	TZ ( $E_{10}/E_{11}$ )	TZ ( $E_{11}/E_{12}$ )	TZ ( $C_{26}/C_{30}$ )	TZ ( $C_{30}/C_{34}$ )
SM-30	23.0	21.3	38.0	31.6
SM-50	21.5	20.0	38.9	32.4
SP-50	20.5	19.2	38.3	32.0
SP-43	22.6	21.5	39.7	33.2
SP-25	12.6	13.5	37.9	32.7
SP-20	14.2	15.5	34.4	28.6
SMP-5	13.5	13.7	33.2	29.2
DB-1ht <sup>b</sup>	17.3	15.6	32.1	27.4
007-65HT <sup>b</sup>	6.9	8.5	31.8	26.4
SOP-75	12.6	14.2	37.8	31.8

<sup>a</sup> Capillary dimensions length 15 m, I.D. 0.32 mm, film thickness 0.2  $\mu\text{m}$ . After conditioning at 380  $^{\circ}\text{C}$ .

<sup>b</sup> Film thickness 0.1  $\mu\text{m}$ .

anes [2] leading to a unique selectivity of the silphenylene unit. Consequently, the proposed equivalence model can only be a relatively rough, though useful estimation.

### 3.3. Separation efficiency

Separation efficiencies of seven silphenylene-siloxane copolymers were calculated as Trennzahl (TZ) from the Grob test and Donike test mixture chromatograms (Table 5). Highest values were found for SM-30, SM-50, SP-50, and SP-43, probably due to their low polarity. More polar phases such as SP-25, SP-20, and SMP-5 exhibit clearly lower separation efficiencies at low temperatures. It is evident from the Grob test chromatograms that the TZ values of  $E_{10}/E_{11}$  were smaller than of  $E_{11}/E_{12}$ , indicating that these components eluted below the MiAOT of the capillary column. Nevertheless the separation efficiencies of these phases were distinctly higher at elevated temperatures (above the MiAOT), as indicated by high TZ values derived from the Donike test components. Furthermore, all silphenylene-siloxane copolymers exhibit similar or slightly superior separation efficiencies compared to the commercially available capillary columns DB-1ht and 007-65HT (see Table 5).

### 3.4. Column bleed

Bulky units incorporated into the polysiloxane

backbone decrease column bleed, since the formation of cyclic oligomers is restricted due to steric hindrance. Thermal gravimetric analysis data demonstrated improved thermal stability of silphenylene-siloxane copolymers compared to polysiloxanes [27].

The column bleed of seven silphenylene-siloxane copolymers measured at 360 and 380  $^{\circ}\text{C}$  are summarized in Table 6. Two commercially available capillary columns and two laboratory-made columns

Table 6  
Column bleed at 360 and 380  $^{\circ}\text{C}$  of seven silphenylene-siloxane copolymers and four polysiloxanes<sup>a</sup>

Stationary phase	Relative bleed (pA) <sup>b</sup>	
	360 $^{\circ}\text{C}$	380 $^{\circ}\text{C}$
SM-30	6.3	16.1
SM-50	11.4	23.9
SP-50	6.6	13.1
SP-43	9.7	16.9
SP-25	10.2	17.0
SP-20	8.9	15.9
SMP-5	12.8	21.7
DB-1ht <sup>c</sup>	4.6	10.3
OV-1	13.4	29.2
007-65HT <sup>c</sup>	15.3	33.7
SOP-75	51.0	74.7

<sup>a</sup> After conditioning at 380  $^{\circ}\text{C}$ , capillary dimensions: length 15 m, I.D. 0.32 mm, film thickness 0.2  $\mu\text{m}$ .

<sup>b</sup> Bleed at elevated temperature minus bleed at 60  $^{\circ}\text{C}$ . Each value represents the mean value of two different capillary columns.

<sup>c</sup> Film thickness 0.1  $\mu\text{m}$ .

coated with polysiloxanes were included for comparative purposes. Reduced column bleed was found for all silphenylene-siloxane copolymers compared to polysiloxanes. Especially SP-50 coated columns exhibits a very low degree of bleed, probably due to its alternating microstructure. On the other side, the alternating copolymer SM-50 offers a higher bleed rate than SM-30, although lowest bleeding levels are expected for copolymers with alternating microstructure [28]. The increased bleeding rate of SM-50 cannot be explained; however, the microstructure may have some impact on column bleed. All copolymers except SM-50 and SP-50 have randomized microstructures as shown by  $^{29}\text{Si}$  NMR [13]. Small amounts of silphenylene units incorporated into the polysiloxane backbone in combination with a randomized microstructure seem to be sufficient to reduce column bleed.

In terms of column bleed the DB-1ht column with 100% dimethyl-polysiloxane is superior to the silphenylene-siloxane copolymers. On the other side, the commercially available column 007-65HT (65% diphenyl, 35% dimethyl-polysiloxane) exhibits striking higher column bleed rates, though this capillary has only half of the film thickness and is dedicated for high-temperature analysis. The laboratory-made capillary columns coated with 100% dimethyl-polysiloxane OV-1 and 75% diphenyl, 25% dimethyl-polysiloxane SOP-75 [5,18] exhibit distinctly higher bleeding rates than all silphenylene-siloxane copolymers. Since all these capillary columns have been prepared with similar deactivation and immobilization procedures, the decreased bleed can be exclusively attributed to the design of the stationary phase and not to improved column deactivation or cross-linking techniques.

An important implication of reduced bleed is a higher maximum allowable operating temperature (MAOT). Expectedly, the MAOTs for all silphenylene-siloxane copolymers lay above 390 °C, although the capillary columns were not tested above this temperature level.

### 3.5. Increase of elution temperature

The elution temperature depends strongly on gas chromatographic conditions complicating a compar-

ison of published data. In this work, the capillary dimensions were standardized and the columns were prepared with the same procedure resulting in a same film thickness. All test chromatograms were performed under standardized gas chromatographic conditions on the same GC instrument.

To monitor the elution temperatures over the complete temperature range, four probes with different chemical functional groups were applied: a fatty acid methyl ester (methyl dodecanoate,  $E_{12}$ ), an *n*-alkane (tetratriacontane,  $C_{34}$ ), a cholesteryl fatty acyl ester (cholesteryl dodecanoate, CE12:0), and a saturated triacylglycerol (tripalmitin, PPP). The elution temperatures of these four probes were plotted against the diphenyl content of four dimethyl, diphenyl-polysiloxanes (see Fig. 4). The data points of each probe,  $E_{12}$ ,  $C_{34}$ , CE12:0, and PPP were fitted with linear regression curves with regression coefficients ranging from  $-0.96194$  (for CE12:0) to  $-0.99731$  (for  $C_{34}$ ). It is evident from this graph that the elution temperatures of all probes decrease with increasing phenyl content. The elution temperatures of the four probes separated on the seven silphenylene-siloxane copolymers were included as solid symbols in Fig. 4 and were plotted against their equivalent diphenyl content calculated with model D. This enables a direct comparison of retention properties of silphenylene-siloxane copolymers and polysiloxanes. It is apparent that the elution temperatures of the four probes are enhanced on all silphenylene-siloxane copolymers compared to polysiloxanes. For example, the replacement of 50% of dimethylsiloxo groups by silphenylene groups (OV-1 and SM-50) results in an increase of the elution temperatures of approximately 15–30 °C. Furthermore it is interesting, that the difference in the elution temperatures rise with increasing temperature ( $\Delta=17$  °C for  $E_{12}$ ;  $\Delta=24$  °C for  $C_{34}$ ;  $\Delta=25$  °C for CE12:0;  $\Delta=28$  °C for PPP).

Similar increased elution temperatures of 15–20 °C have already been reported for silphenylene-siloxane copolymers, sildiphenyl ether-siloxane copolymers, and carboran-siloxane copolymers [11,12]. A possible explanation may be steric interactions of the analytes with the planar phenylene ring system. For example, the linear *p*-xylene ring system can gain closer physical proximity to the backbone and

interacts more strongly with a silphenylene-dimethylsiloxane copolymer [3].

### 3.6. Minimum allowable operating temperature

Below the glass transition temperature a polymer is brittle and hard, restricting the diffusion of gaseous analyte molecules into the stationary phase during the chromatographic process which is indicated by misshapen peaks. Above the glass transition temperature the viscosity of a polymer increases and diffusion is enabled. The MiAOTs of the silphenylene-siloxane copolymers SM-30, SM-50, and SP-50 are below 40 °C as these polymers have glass transition temperatures far below this working range. For the copolymers with intermediate polarity SP-43, SP-25, and SP-20 glass transition temperatures were found to be in the range between 13 and 21 °C. As expected, the glass transition temperature increase with increasing phenyl content [29]. Increased MiAOTs are indicated by distorted peak shapes of early eluting components of the Grob test chromatograms of SP-25, SP-20, and SMP-5 (Fig. 1). Therefore, the MiAOTs of these polymers are approximately 100 °C. This is also the reason why the separation efficiency increases with temperature (see TZ for SP-25, SP-20, and SMP-5 in Table 5), although the TZ values generally decrease with increasing temperature.

## 4. Conclusions

Silphenylene-siloxane copolymers have several unique properties, which are caused by the phenylene group inserted into the polysiloxane backbone.

(i) The impact of the silphenylene unit on the selectivity can be described by the assumption that a silphenylene unit is equivalent with two dimethylsiloxy groups and one-half of a diphenylsiloxy group.

(ii) The increased thermal stability caused by the backbone stiffing phenylene group results in low column bleeding rates and increased MAOTs.

(iii) The silphenylene unit increases the elution

temperatures of analytes of 15–30 °C compared to equivalent polysiloxanes. Thus, the advantage of decreased column bleed is partly lost by enhanced elution temperatures.

(iv) Increased glass transition temperatures result in elevated MiAOTs.

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